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Stereochemical Selectivity during the Formation of $CH_2RCH_2CHRCH_2$– Branches in the Free Radical Initiated Polymerization of Monosubstituted Vinyl Monomers

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ABSTRACT: Isolated butyl branches in low-density polyethylene are formed by an intrachain radical rearrangement that is followed by repeated addition of ethylene without further rearrangement. The analogous intramolecular radical rearrangement in a monosubstituted vinyl chain that is terminated by $-CHRCH_2CHRCH_2\dot{C}HR$, followed by the repeated addition of $CHR{=}CH_2$, produces an isolated $-CH_2CHRCH_2CH_2R$ branch. The probability of this rearrangement is strongly influenced by the stereochemistry of the diad denoted by asterisks in the fragment $-CHR^*CH_2CHR^*CH_2\dot{C}HR$. The rearrangement is more likely in chains that have a meso diad at this position. There is an increase in selectivity for meso diads as η increases. Here η is the first-order statistical weight for a trans placement at a bond in the main chain.

The free radical initiated polymerization of ethylene at high pressure produces a branched polymer. Intermolecular hydrogen atom abstraction is responsible for the formation of long branches, which can contain a number of bonds comparable with that found in the main chain.[1,2] Intramolecular hydrogen atom abstraction via a cyclic intermediate is the crucial step in the formation of short branches.[3] The intramolecular radical rearrangement can be written as

$$-(CH_2)_kCH_2(CH_2)_{j-1}\dot{C}H_2 \rightarrow -(CH_2)_k\dot{C}H(CH_2)_{j-1}CH_3 \qquad (1)$$

The butyl branch is the most frequently reported short branch in low-density polyethylene,[4-14] but other short branches have also been identified.[4-15] An isolated butyl branch is formed if $j = 4$ and the intramolecular radical rearrangement in eq 1 is followed by addition of several molecules of ethylene without further rearrangement.[3,16] A complex branch can be formed if a second intramolecular radical rearrangement takes place after the addition of only one or two molecules of ethylene.[16-18]

An intramolecular radical rearrangement with $j = 4$ is depicted in a somewhat different manner in Figure 1. The hydrogen atom that will be abstracted is denoted by H*. Figure 1 and eq 1 describe the same intramolecular radical rearrangement if $R = H$ and $j = 4$. However, if $R \neq H$, Figure 1 depicts intramolecular radical rearrangements in monosubstituted vinyl polymers. For example, if $R = Cl$, Figure 1 describes the intramolecular radical rearrangement that leads to the formation of 2,4-dichloro-*n*-butyl branches, which are second in occurrence only to chloromethyl branches in poly(vinyl chloride).[19] The first defined diad at the growing chain end in Figure 1A is a meso diad, but it is replaced by a racemic diad in Figure 1B.

The R substituent affects the rates of the two intramolecular radical rearrangements because it alters the inherent reactivity of H* and also influences the probability that the chain end will adopt a conformation that brings the reactive chain end and H* into a suitable juxtaposition. Both factors need be considered in a comparison of two chains that have different R substituents. Conformational control is the only important factor if the interest is in the relative rates of the two intramolecular radical rearrangements under circumstances where both chains have the same R substituents. At issue is whether the stereochemical composition at the reactive chain end has an influence on the probability for the formation of an isolated $-CH_2CHRCH_2CH_2R$ branch. A rotational isomeric state analysis can easily demonstrate that the intramolecular radical rearrangement depicted in Figure 1A is generally favored over that in Figure 1B. The selectivity may be greater than a factor of 10.

Rotational Isomeric State Treatment

Configuration partition functions for the monosubstituted vinyl polymers are obtained with minor modification of the rotational isomeric state treatment developed by Flory et al.[20] The configuration partition functions are

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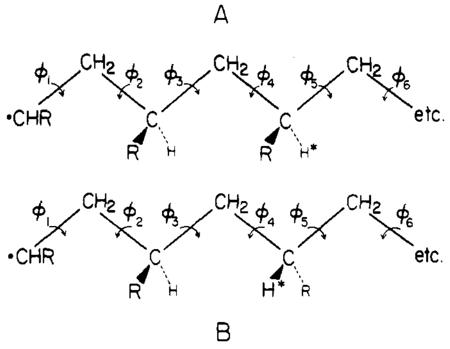

Figure 1. Two $-CH_2CHRCH_2CHRCH_2\dot{C}HR$ chains with different stereochemical compositions for the defined diad.

denoted by Z_m and Z_r, respectively, for the chains in parts A and B of Figure 1. They can be written as

$$Z_m = \mathbf{U}_1\mathbf{U}_2\mathbf{U}'\mathbf{U}_m''\mathbf{U}'[\nu_1 \quad \nu_2 \quad \nu_3]^{\mathrm{T}} \tag{2}$$

$$Z_r = \mathbf{U}_1\mathbf{U}_2\mathbf{U}'\mathbf{U}_r''\mathbf{U}'[\nu_1 \quad \nu_2 \quad \nu_3]^{\mathrm{T}} \tag{3}$$

where

$$\mathbf{U}_1 = [\eta^* \quad 1 \quad \eta^*] \tag{4}$$

$$\mathbf{U}_2 = \begin{bmatrix} \eta\omega'' & 1 & \tau\omega' \\ \eta & 1 & \tau \\ \eta & \omega' & \tau\omega'' \end{bmatrix} \tag{5}$$

$$\mathbf{U}' = \begin{bmatrix} \eta & 1 & \tau \\ \eta & \omega & \tau \\ \eta & 1 & \tau\omega \end{bmatrix} \tag{6}$$

$$\mathbf{U}_m'' = \begin{bmatrix} \eta\omega'' & 1 & \tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\omega' & \omega' & \tau\omega\omega'' \end{bmatrix} \tag{7}$$

$$\mathbf{U}_r'' = \begin{bmatrix} \eta & \omega' & \tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega' & \omega & \tau\omega'^2 \end{bmatrix} \tag{8}$$

and T as a superscript denotes the transpose.

Statistical weight matrices $\mathbf{U}_m''$ and $\mathbf{U}_r''$, which are for the CH_2–CHR bond in meso and racemic diads, respectively, are taken directly from Flory et al.[20] The matrix $\mathbf{U}'$, which is for the CHR–CH_2 bond, differs from $\mathbf{U}'$ of Flory et al. only in that the statistical weight for the gg and $\bar{g}\bar{g}$ states is assigned as ω, rather than as zero. This change is made because gg or $\bar{g}\bar{g}$ placements at bonds 2 and 3 are required in conformations conducive to the intramolecular radical rearrangement of interest. Since these conformations are of low probability, they can be ignored in the calculation of statistical mechanical averages of properties that are dominated by much more probable chain conformations. The mean square unperturbed end-to-end distance is an example of such a property. However, the property of current interest is determined by the occasional occupancy of relatively improbable conformations. Null elements in $\mathbf{U}'$ cannot be tolerated in the present work. Matrix $\mathbf{U}_2$ differs from $\mathbf{U}_m''$ by the deletion of two ω and two ω'. The deleted statistical weights arise from second-order interactions involving the methylene group that would precede the terminal ·CHR after head-to-tail reaction of the chain end with one molecule of $CHR{=}CH_2$. The statistical weight denoted by η^* in $\mathbf{U}_1$ arises from the first-order interaction of a main-chain carbon atom and the R at the terminal ·CHR. A reasonable approximation for η^* is $\sigma\eta$, where σ is the statistical weight for the first-order interaction in linear polyethylene. The numerical values for ν_1, ν_2, and ν_3 depend on the degree of polymerization and stereochemical composition of the remainder of the chain. The three ν_i can be calculated from $\mathbf{U}'$, $\mathbf{U}_m''$, and $\mathbf{U}_r''$ after the degree of polymerization and stereochemical sequence are specified.

Table I
Parameter Sets[a]

polymer	η	τ	ω	ω'	ω''	ref
poly(vinyl bromide)	1.3	0.43	0.015	0.035	0.0024	26
polystyrene	1.56	0	0.046	0.046	0.046	22
poly(alkyl vinyl ether)	2.1	0.43	0.035	0.12	0.16	23
poly(*N*-vinylcarbazole)	2.5	0	0.16	0.35	0.09	25
poly(methyl vinyl ketone)	2.7	0	0.05	0.02	0.008	24
poly(vinyl chloride)	4.2	0.45	0.032	0.071	0.032	21
average	2.4	0.22	0.056	0.11	0.056	

[a] $\eta^* = 0.43\eta$ in each case.

The intramolecular radical rearrangement requires the proper conformation at bonds 2, 3, and 4[16] so that the reactive chain end is sufficiently close to H* and $C{-}H^*\cdots\dot{C}HR{-}$ approximates "three-in-a-line" geometry. These conformations are ggt and $\bar{g}\bar{g}g$ for the structure in Figure 1A. Chains in which the placements at bonds 2, 3, and 4 are ggt or $\bar{g}\bar{g}g$ contribute terms M_1 and M_2, respectively, to Z_m. The probability for a reactive conformation in Figure 1A is

$$p_m = (M_1 + M_2)/Z_m \tag{9}$$

where

$$M_1 = \eta\omega(\eta^* + 1 + \eta^*\omega')(\eta\nu_1 + \nu_2 + \tau\nu_3) \tag{10}$$

$$M_2 = \tau^2\omega\omega'(\eta^*\omega' + 1 + \eta^*\omega'')(\eta\nu_1 + \omega\nu_2 + \tau\nu_3) \tag{11}$$

The reactive chains in Figure 1B have ggg or $\bar{g}\bar{g}t$ placements at bonds 2, 3, and 4. Chains with these conformations at bonds 2–4 contribute terms R_1 and R_2, respectively, to Z_r. The probability for a reactive conformation of the chain in Figure 1B is

$$p_r = (R_1 + R_2)/Z_r \tag{12}$$

where

$$R_1 = (\eta^* + 1 + \eta^*\omega')(\eta\nu_1 + \tau\nu_2 + \omega\nu_3) \tag{13}$$

$$R_2 = \tau^2\eta\omega\omega''(\eta^*\omega' + 1 + \eta^*\omega'')(\eta\nu_1 + \tau\nu_2 + \nu_3) \tag{14}$$

Numerical Results for Selected Monosubstituted Vinyl Polymers

The range of behavior expected for monosubstituted vinyl polymers can be defined by using the six parameter sets collected in Table I. These sets are the statistical weights, evaluated at 300 K, for rotational isomeric state models of poly(vinyl chloride),[21] polystyrene,[22] poly(alkyl vinyl ether),[23] poly(methyl vinyl ketone),[24] poly(*N*-vinylcarbazole),[25] and poly(vinyl bromide).[26] The polymers are listed in Table I in order of increasing η.

The relative ease with which the two chains depicted in Figure 1 can form an isolated $-CH_2CHRCH_2CH_2R$ branch is under conformational control. The crucial quantity is p_m/p_r. This ratio would be one if conformations conducive to the intramolecular radical rearrangement were equally probable in the two chains depicted in Figure 1. The ratio is greater than one if reactive conformations are more easily adopted by the chain with the meso diad. The second column in Table II presents numerical values of p_m/p_r when $\nu_1 = \nu_2 = \nu_3 = 1$. This set of ν_i would be correct if $\phi_1 - \phi_5$ were independent of $\phi_6 - \phi_n$, where n is the number of bonds in the chain. The p_m/p_r are all greater than one, and in one case p_m/p_r is greater than ten. The

Table II
Numerical Values of p_m/p_r

polymer	$\nu_i = 1$	ν_i from $\mathbf{U}_m''\mathbf{J}$ or $\mathbf{U}_r''\mathbf{J}^a$
poly(vinyl bromide)	2.5	2.7–3.3
polystyrene	3.4	2.9–4.3
poly(alkyl vinyl ether)	3.9	3.5–4.8
poly(*N*-vinylcarbazole)	6.2	5.6–8.4
poly(methyl vinyl ketone)	6.8	5.5–9.6
poly(vinyl chloride)	12	10–20

[a] $\mathbf{J} = [1\ 1\ 1]$.

results in the second column of Table II suggest branching is more likely if the first defined diad at the chain end is meso.

Of course, the assumed independence of bonds 1–5 from bonds 6–n is unrealistic. Bonds in monosubstituted vinyl polymers are subject to interdependent rotation potentials. Therefore it is necessary to ascertain whether the large values of p_m/p_r in the second column of Table II are artifacts that result from the unrealistic assignment of the ν_i. Bond 6 will have a greater influence on bonds 1–5 than will bonds 7–n. The rotation potential at bond 6 depends on the nature of the second diad in the chain. The influence of this bond can be assessed if p_m and p_r are recalculated by using

$$[\nu_1 \quad \nu_2 \quad \nu_3]^{\mathrm{T}} = \mathbf{U}_m''[1 \quad 1 \quad 1]^{\mathrm{T}} \tag{15}$$

and

$$[\nu_1 \quad \nu_2 \quad \nu_3]^{\mathrm{T}} = \mathbf{U}_r''[1 \quad 1 \quad 1]^{\mathrm{T}} \tag{16}$$

Equation 15 is appropriate if the two diads at the end of the chain are meso–meso or racemic–meso, and eq 16 would be used if these two diads are meso–racemic or racemic–racemic. These assignments for the ν_i specify four additional p_m/p_r for each polymer.

The range of the p_m/p_r obtained with eq 15 and 16 is given in the last column of Table II. For five of the six polymers, the p_m/p_r calculated with $\nu_1 = \nu_2 = \nu_3 = 1$ falls in the range specified by the more realistic ν_i. In the remaining case, poly(vinyl bromide), utilization of the more realistic ν_i brings about a small increase in p_m/p_r. Use of the more realistic ν_i does not result in p_m/p_r near one. Instead it tends to increase slightly the values of p_m/p_r. Typical monosubstituted vinyl polymers can be expected to have large values of p_m/p_r. A meso diad at the chain end enhances the probability for the formation of an isolated $-CH_2CHRCH_2CH_2R$ branch.

An Instructive Approximation

In each of the parameter sets in Table I, η is the only statistical weight that is greater than one. Even though η is only 30% greater than 1 in some chains, it nevertheless is useful to examine the limiting form for p_m/p_r when $\eta \gg 1$, with the remaining statistical weights being no larger than 1. The limiting forms for Z_m and Z_r are

$$Z_m \rightarrow \eta^4\eta^*\omega''\nu_1(1 + \omega'') \tag{17}$$

$$Z_r \rightarrow \eta^4\eta^*\nu_1(1 + \omega'') \tag{18}$$

and the limiting p_m and p_r are

$$p_m \rightarrow \omega(1 + \omega')[\eta^2\omega''(1 + \omega'')]^{-1} \tag{19}$$

$$p_r \rightarrow \tau^2\omega\omega''(\omega' + \omega'')[\eta^2(1 + \omega'')]^{-1} \tag{20}$$

The dominance of η ensures that chain conformations with a trans placement at bond 5 are much more probable than conformations with a gauche placement. Equation 19 gives the probability for the ggt conformation at bonds 2–4 when η is large. The $\bar{g}\bar{g}g$ conformation, which along with ggt contributes to eq 9, is irrelevant when η is very large. Similarly, eq 20 specifies the probability for the $\bar{g}\bar{g}t$ conformation in the limit of very large η. Under these conditions, the $\bar{g}\bar{g}t$ conformation completely dominates the ggg conformation, although the latter can be important at smaller η, as shown by eq 12. The limiting form for the desired ratio is

$$p_m/p_r \rightarrow (1 + \omega')[\tau^2(\omega'')^2(\omega' + \omega'')]^{-1} \tag{21}$$

which depends strongly on τ and ω''. It also depends on ω' unless $\omega' \ll \omega''$. If τ, ω', and ω'' are much less than one, as they are for the six parameter sets in Table I, the limiting form in eq 21 is greater than one. Indeed, the limiting value of p_m/p_r is much greater than one if $\tau\omega'' \ll 1$, as is usually the case. The *smallest* limiting p_m/p_r specified by the parameters in Table I is greater than 1000.

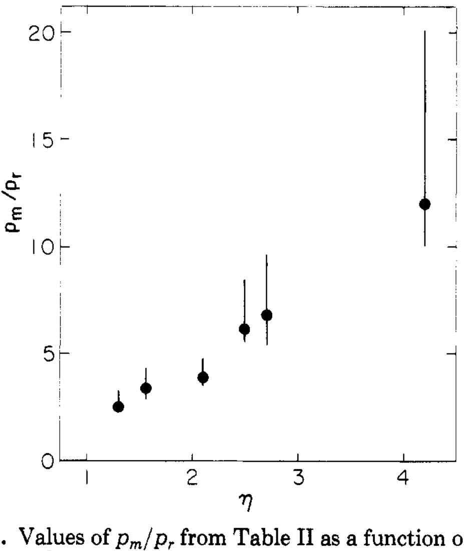

Figure 2. Values of p_m/p_r from Table II as a function of η. The filled circles denote p_m/p_r when $\nu_1 = \nu_2 = \nu_3 = 1$, and the bars denote the range when the ν_i are specified by $\mathbf{U}_m''\mathbf{J}$ and $\mathbf{U}_r''\mathbf{J}$.

The data collected in Table II are depicted as a function of η in Figure 2. Clearly there is a tendency for p_m/p_r to increase as η increases. Even though η is never greater than 4.2 and the p_m/p_r are orders of magnitude smaller than the limits specified by eq 21, the limiting form provides a useful rationalization of the results. The value of p_m/p_r is driven toward the large limit as η increases.

The scope of the conclusion that $p_m/p_r > 1$ is more forcefully illustrated by considering the consequences of individual variations in each of the statistical weights. It is useful to examine variations about a reference set. The reference set will be taken to be the averages of the statistical weights for the six monosubstituted vinyl polymers in Table I. These averages are found in the last line of Table I.

Figure 3 depicts changes in p_m/p_r when η, τ, ω, ω', and ω'', in turn, are varied about the reference value. The value of p_m/p_r is far more sensitive to η than to any of the other statistical weights. As η increases, the value of p_m/p_r is driven toward the enormous limit specified by eq 21. The value of p_m/p_r increases slightly as τ or ω'' decreases. These changes are in the direction expected (but not of the size expected) from the appearance of $(\tau\omega'')^2$ in the denominator of eq 21. Still smaller changes are seen upon variation of ω or ω'.

The intramolecular radical rearrangement that can produce an isolated $-CH_2CHRCH_2CH_2R$ branch occurs preferentially in chains that have a meso diad at the end and ggt placements at bonds 2–4. It is expected that p_m/p_r

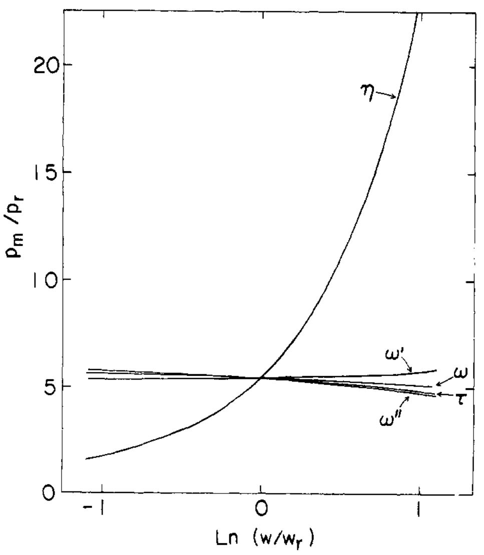

Figure 3. Values of p_m/p_r when the statistical weight denoted by w is varied about its reference value w_r. The assignment of w is shown for each curve.

should generally be greater than one for monosubstituted vinyl polymers.

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Organophosphazenes. 19. Copolymerization of 2-(α-Ethoxyvinyl)pentafluorocyclotriphosphazene with Styrene and Methyl Methacrylate[1]

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ABSTRACT: The novel phosphazene, 2-(α-ethoxyvinyl)pentafluorocyclotriphosphazene ($N_3P_3F_5C(OC_2H_5)=CH_2$) undergoes radical copolymerization with styrene and methyl methacrylate. The styrene system was examined in detail, with flame retardant copolymers having up to 43.7% phosphazene content being obtained. Reactivity ratios for the styrene–(α-ethoxyvinyl)phosphazene copolymerization have been calculated by several methods. An examination of the Alfrey–Price parameters for the phosphazene indicates that the major perturbation of the olefinic center is through the σ-electron-withdrawing effect of the phosphazene. The copolymer molecular weights decrease with increasing phosphazene content. The thermal decomposition of the copolymers is a two-step process, with the phosphazene being involved in the first step.

Introduction

Recent work in our laboratories has been devoted to the synthesis and reactions of organofunctional phosphazenes.[2] Of particular interest is the preparation of polymeric systems derived from organofunctional phosphazene monomers.[2-4] We originally demonstrated the feasibility of such an approach by reporting the copolymerization of 2-(α-methylvinyl)pentafluorocyclotriphosphazene, $N_3P_3F_5C(CH_3)_3=CH_2$, with styrene and vinyl benzene chloride.[3] These copolymers met our initial criteria of being hybrid organic–inorganic polymers, exhibiting significant flame retardant behavior[3] and having a functionalized surface due to the presence of the halophosphazene.[4] There are, however, problems with the inorganic monomer that are related to the polarity induced in the olefin by the highly electron-withdrawing[5-7] phosphazene substituent. The olefin polarity causes difficulties in the preparation of the monomer[8,9] and favors termination in copolymerization reactions.[3] We have recently reported the preparation of a new alkenylphosphazene monomer system derived from vinyl ethers in which it was proposed that the electron-donor effect of the alkoxy group toward the olefin would counterbalance the electron-withdrawing effect of the phosphazene.[9,10] This expectation was realized in the